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PATENT ABSTRACTS OF JAPAN

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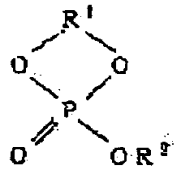
(71)Applicant : MITSUBISHI CHEM CORP
(72)Inventor : SHIMA KUNIHISA
ISHIGAKI KENICHI
YASUKAWA SHIGEKI
MORI SHOICHIRO

(54) ELECTROLYTE FOR LITHIUM BATTERY

(57)Abstract:
PROBLEM TO BE SOLVED: To provide an organic solvent electrolyte having self-extinguishing capability by dissolving a lithium salt of solute in a mixed solvent containing a cyclic phosphate and a cyclic carbonate in the specified ratio.
SOLUTION: As a lithium salt used as a solute, LiPF6, or the like is listed. The concentration of the lithium salt is 0.1-1.5 mole/1. The mixed solvent contains 20-55 vol.% of cyclic phosphate represented by the formula and 10-80 vol.% of cyclic carbonate. In the formula, R1 represents a 2-8C alkylene group, R2 represents a 1-4C alkyl group. The cyclic phosphate has self-extinguishing capability, and its capability is increased with decrease in the number of carbon atoms and the content of hydrogen. Preferably, methyl ethylene phosphate, ethylene phosphate, and the like are listed. As the cyclic carbonate, ethylene carbonate, propylene carbonate, and the like are listed.



LEGAL STATUS

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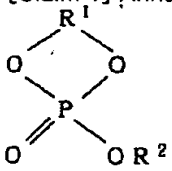
CLAIMS

[Claim(s)]
[Claim 1] Annular phosphoric ester shown by the (a) formula (1) in the lithium salt of a solute. [Formula 1]



(1)

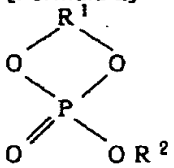
R1 expresses the alkylene machine of carbon numbers 2-8 among [formula, and R2 expresses the alkyl group of carbon numbers 1-4.]
Capacity [20 to 55] %, and (b) annular carbonate: The electrolytic solution for lithium cells which dissolved in the mixed solvent containing 10 - 80 capacity %.
[Claim 2] Decomposition liquid for lithium cells according to claim 1 whose annular carbonate (b) is the compound chosen from the ethylene carbonate and the propylene carbonate.
[Claim 3] The electrolytic solution for lithium cells according to claim 1 whose annular phosphoric ester (a) shown by the formula (1) is the compound chosen from a phosphoric-acid methyl ethylene and phosphoric-acid ethyl ethylene.
[Claim 4] a mixed solvent — (— a —) — a formula — (— one —) — being shown — having — annular — phosphoric ester — 20 — - — 55 — capacity — % — (— b —) — annular — a carbonate — 30 — - — 75 — capacity — % — and — (— c —) — one — two — - — dimethoxyethane — and — a dimethyl carbonate — choosing — having had — a compound — five — - — 15 — capacity — % — mixture — it
[Claim 5] the lithium salt of a solute — LiPF6 it is — the electrolytic solution for lithium cells according to claim 1

[Translation done.]

* NOTICES *

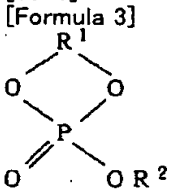
DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[The technical field to which invention belongs] this invention has self-extinguishing and relates to the electrolytic solution for lithium cells excellent in safety.
[0002]
[Description of the Prior Art] In recent years, the lithium cell using the organic-solvent electrolytic solution is widely used as a power supply of high-energy density with the miniaturization of electronic equipment, and carrying-izing. This organic-solvent electrolytic solution is a low viscosity solvent to an ethylene carbonate, a propylene carbonate, gamma-butyrolactone, etc. as a high dielectric constant solvent. the solvent which mixed dimethyl-carbonate, ethyl-carbonate methyl, diethyl carbonate, 1, and 2-dimethoxyethane etc. — a solute (electrolyte) LiPF6, LiBF4, LiCF3 SO3, and LiN (CF3 SO2)2 etc. — what mixed lithium salt is used
[0003]
[Problem(s) to be Solved by the Invention] The solvent currently used for such the electrolytic solution is an inflammable inflammable high solvent, and when the electrolytic solution spills liquid by the pressure buildup inside a cell, or mechanical destruction of a cell, it has the danger of carrying out ignition combustion. Moreover, development of the object for power storage or the large-sized cell for electric vehicles is also furthered, and the safe disposition top, such as flameproofing of the electrolytic solution, is called for. this invention solves the above technical problem and aims at offer of the organic-solvent electrolytic solution which has self-extinguishing.
[0004]
[Means for Solving the Problem] this invention is cyclic-phosphoric-acid ester shown by the (a) formula (1) in lithium salt as a solute. [0005]
[Formula 2]



(1)

[0006] R1 expresses the alkylene machine of carbon numbers 2-8 among [formula, and R2 expresses the alkyl group of carbon numbers 1-4.]
The electrolytic solution for lithium cells which dissolved in the mixed solvent containing 20 to 55 capacity %, and the (b) annular carbonate 10 - 80 capacity % is offered.
[0007]
[Function] Cyclic-phosphoric-acid ester has self-extinguishing, and gives self-extinguishing to the electrolytic solution for lithium cells by making the electrolytic solution contain.
[0008]
[Embodiments of the Invention]
Lithium salt as a solute: As the electrolyte used for the electrolytic solution of this invention LiPF6, LiBF4, LiClO4, LiAsF6, and LiSbF6, LiCF3 SO3, LiN (CF3 SO2)2, and LiN (CF3 CF2 SO2)2, LiN (CF3 SO2) (CF3 3 (CF2) SO2), LiN (CF3 3 (CF2) SO2)2, LiC (CF3 SO2)3, and LiC (CF3 CF2 SO2)3 etc. — lithium salt can be used The lithium salt concentration in the electrolytic solution can be used by the 0.1-1.5 mols [/l.] density range.
[0009] Mixed solvent: It is cyclic-phosphoric-acid ester shown by the (a) formula (1) as a solvent in this invention.
[0010]
[Formula 3]



(1)

[0011] R1 expresses the alkylene machine of carbon numbers 2-8 among [formula, and R2 expresses the alkyl group of carbon numbers 1-4.]
The mixed solvent containing 20 to 55 capacity %, and the (b) annular carbonate 10 - 80 capacity % is used.
(a) Cyclic-phosphoric-acid ester : an autolysis-slaking operation of cyclic-phosphoric-acid ester (a) is the alkylene machine R1, so that there are few the carbon and the hydrogen contents in cyclic-phosphoric-acid ester. And alkyl group R2 It is so large that it is small. Therefore, alkylene machine R1 2-8 pieces are desirable and a carbon number is an alkyl group R2. 1-4 pieces of a carbon number are desirable. Alkylene machine R1 If it carries out, an ethylene, a propylene machine, a trimethylene machine, a butylene machine, an isobutylene machine, a tetramethylen machine, a pentamethylene machine, a trimethylethylene machine, a hexamethylene machine, a tetramethyl ethylene, a

heptamethylene machine, an octamethylene machine, etc. are mentioned. Moreover, alkyl group R2 If it carries out, a methyl group, an ethyl group, n-propyl group, an isopropyl machine, n-butyl, a sec-butyl, t-butyl, an isobutyl machine, etc. are mentioned.

[0012] As an example of cyclic-phosphoric-acid ester (a), it is a phosphoric-acid ethylene methyl. Phosphoric-acid ethylene ethyl, a phosphoric-acid ethylene-n-propyl, a phosphoric-acid ethylene isopropyl, Phosphoric-acid ethylene-n-butyl, phosphoric-acid ethylene-sec-butyl, phosphoric-acid ethylene-t-butyl, A phosphoric-acid propylene methyl, phosphoric-acid propylene ethyl, a phosphoric-acid propylene-n-propyl, A phosphoric-acid propylene isopropyl, phosphoric-acid propylene-n-butyl, phosphoric-acid propylene-sec-butyl, Phosphoric-acid propylene-t-butyl, a phosphoric-acid trimethylene methyl, phosphoric-acid trimethylene ethyl, A phosphoric-acid trimethylene-n-propyl, a phosphoric-acid trimethylene isopropyl, Phosphoric-acid trimethylene-n-butyl, phosphoric-acid trimethylene-sec-butyl, Phosphoric-acid trimethylene-t-butyl, a phosphoric-acid butylene methyl, phosphoric-acid butylene ethyl, A phosphoric-acid butylene-n-propyl, a phosphoric-acid butylene isopropyl, phosphoric-acid butylene-n-butyl, Phosphoric-acid butylene-sec-butyl, phosphoric-acid butylene-t-butyl, A phosphoric-acid isobutylene methyl, phosphoric-acid isobutylene ethyl, a phosphoric-acid isobutylene-n-propyl, A phosphoric-acid isobutylene isopropyl, phosphoric-acid isobutylene-n-butyl, Phosphoric-acid isobutylene-sec-butyl, phosphoric-acid isobutylene-t-butyl, Phosphoric-acid tetramethylen memory, phosphoric-acid tetramethylen ethyl, a phosphoric-acid tetramethylen-n-propyl, A phosphoric-acid tetramethylen isopropyl, phosphoric-acid tetramethylen-n-butyl, Phosphoric-acid tetramethylen-sec-butyl, phosphoric-acid tetramethylen-t-butyl, A phosphoric-acid pentamethylene methyl, phosphoric-acid pentamethylene ethyl, a phosphoric-acid pentamethylene-n-propyl, A phosphoric-acid pentamethylene isopropyl, phosphoric-acid pentamethylene-n-butyl, Phosphoric-acid pentamethylene-sec-butyl, phosphoric-acid pentamethylene-t-butyl, A phosphoric-acid trimethylethylene methyl, phosphoric-acid trimethylethylene ethyl, A phosphoric-acid trimethylethylene-n-propyl, a phosphoric-acid trimethylethylene isopropyl, Phosphoric-acid trimethylethylene-n-butyl, phosphoric-acid trimethylethylene-sec-butyl, Phosphoric-acid trimethylethylene-t-butyl, a phosphoric-acid hexamethylene methyl, Phosphoric-acid hexamethylene ethyl, a phosphoric-acid hexamethylene-n-propyl, A phosphoric-acid hexamethylene isopropyl, phosphoric-acid hexamethylene-n-butyl, Phosphoric-acid hexamethylene-sec-butyl, phosphoric-acid hexamethylene-t-butyl, A phosphoric-acid tetramethyl ethylene methyl, phosphoric-acid tetramethyl ethylene ethyl, A phosphoric-acid tetramethyl ethylene-n-propyl, a phosphoric-acid tetramethyl ethylene isopropyl, Phosphoric-acid tetramethyl ethylene-n-butyl, phosphoric-acid tetramethyl ethylene-sec-butyl, Phosphoric-acid tetramethyl ethylene-t-butyl, a phosphoric-acid heptamethylene methyl, Phosphoric-acid heptamethylene ethyl, a phosphoric-acid heptamethylene-n-propyl, A phosphoric-acid heptamethylene isopropyl, phosphoric-acid heptamethylene-n-butyl, Phosphoric-acid heptamethylene-sec-butyl, phosphoric-acid heptamethylene-t-butyl, A phosphoric-acid octamethylene methyl, phosphoric-acid octamethylene ethyl, a phosphoric-acid octamethylene-n-propyl, A phosphoric-acid octamethylene isopropyl, phosphoric-acid octamethylene n-butyl, phosphoric-acid octamethylene-sec-butyl, phosphoric-acid octamethylene-t-butyl, etc. are mentioned. These are independent, or two or more sorts can be mixed and they can be used.

[0013] (b) Annular carbonate : as an annular carbonate, an ethylene carbonate, a propylene carbonate, a carbonic acid butylene, a carbonic acid isobutylene, carbonic acid trimethylene, a carbonic acid trimethylethylene, carbonic acid tetramethyl ethylene, dimethyl-carbonate trimethylene, etc. are mentioned. These are independent, or two or more sorts can be mixed and they can be used.

[0014] (c) Other solvents : out of using annular phosphoric ester (a) and an annular carbonate (b) as a mixed solvent, you may mix and use solvents other than annular phosphoric ester and an annular carbonate (c) for the improvement in electric conductivity of the electrolytic solution. solvent 5-15 capacity % In this case, as for the amount of annular phosphoric ester, 20 to 55 capacity % and 30 to annular carbonate 75 capacity %, and (c) others should just be contained. By making it such a range, electric conductivity is high and can obtain the electrolytic solution for lithium cells which was excellent in self-extinguishing.

[0015] As solvents other than annular phosphoric ester and an annular carbonate A dimethyl carbonate, an ethyl-carbonate methyl, diethyl carbonate, a carbonic acid dipropyl, A carbonic acid diisopropyl, carbonic acid methylpropyl, a methyl carbonate isopropyl, Chain-like carbonates, such as an ethyl-carbonate propyl and an ethyl-carbonate isopropyl 1, 2-dimethoxyethane, 1, 2-diethoxy ethane, 1-ethoxy-2-methoxyethane, Chain-like ether, such as 1, 2-dipropoxy ethane, 1, 2-JIISO propoxy ethane, 1, and 2-dibutoxy ethane, A tetrahydrofuran, a methyl tetrahydrofuran, a tetrahydropyran, Cyclic ether, such as a methyl tetrahydropyran and a dioxane, methyl acetate, Ethyl acetate, propyl acetate, a methyl propionate, an ethyl propionate, Carboxylates, such as gamma-butyrolactone, beta-butyrolactone, delta-valerolactone, and gamma-valerolactone Amides, such as a dimethylformamide and a dimethylacetamide, a sulfurous-acid dimethyl, Sulfites, such as a sulfurous-acid diethyl, sulfurous-acid ethylene, and a sulfurous-acid propylene Sulfates, such as a dimethyl sulfate, a diethyl sulfate, sulfuric-acid ethylene, and a sulfuric-acid propylene, It is independent, or two or more sorts can be mixed and nitril, such as sulfones, such as sulfoxides, such as dimethyl sulfoxide and a diethyl sulfoxide, a dimethyl sulfone, a diethyl sulfone, and a sulfolane, an acetonitrile, and a propionitrile, can also be used. 1, 2-dimethoxyethane, and a dimethyl carbonate are desirable also in these.

[0016]

[Example] Hereafter, an example explains this invention in detail. In addition, evaluation is based on the following method.

10 minutes or more were dipped in the beaker into which the electrolytic solution went the glass fiber filter paper of the shape of a strip of paper with self-extinguishing evaluation of the electrolytic solution and electric conductivity measurement width of face of 15mm, a length [of 300mm], and a thickness of 0.19mm. Except for the superfluous electrolytic solution, the end of a glass fiber filter paper was gathered with a clip from the glass fiber filter paper on the edge of a beaker, and it hung to the perpendicular. Time until it lights and carries out autolysis slaking to this soffit with a writer was measured. Moreover, about the electric conductivity (25 degrees C) of the electrolytic solution, it measured using the electric conductivity meter.

[0017] LiPF6 of the amount which serves as concentration of 1.0 mols/l. at the mixed solvent which made each capacity % of example 1 ethylene carbonate (EC), 1, 2-dimethoxyethane (DME), and a phosphoric-acid methyl ethylene (MEP) 40 capacity %, ten capacity %, and 50 capacity % Self-extinguishing and electric conductivity were measured about the electrolytic solution which dissolved. A result is shown in Table 1.

[0018] LiPF6 of the amount which serves as concentration of 1.0 mols/l. at the mixed solvent which made capacity % of example 2EC, and DME and MEP 60 capacity %, ten capacity %, and 30 capacity % Self-extinguishing and electric conductivity were measured about the electrolytic solution which dissolved. A result is shown in Table 1.
[0019] LiPF6 of the amount which serves as concentration of 1.0 mols/l. at the mixed solvent which made capacity % of example of comparison 1EC, and DME and MEP 80 capacity %, ten capacity %, and ten capacity % Self-extinguishing and electric conductivity were measured about the electrolytic solution which dissolved. A result is shown in Table 1.
[0020] the example 2 of comparison — LiPF6 of the amount which serves as concentration of 1.0 mols/l. at the mixed solvent which made capacity % of EC and DME 90 capacity % and ten capacity % Self-extinguishing and electric conductivity were measured about the electrolytic solution which dissolved. A result is shown in Table 1.
[0021]
[Table 1]

表　1

	混合溶媒			評価	
	EC (容積%)	DME (容積%)	MEP (容積%)	自己消火性	電導度 (mS/cm)
実施例1	40	10	50	1秒以内に消火	6.9
実施例2	60	10	30	3秒で消火	7.1
比較例1	80	10	10	消火せず	7.5
比較例2	90	10	0	消火せず	10.6

EC：エチレンカーボネート

DME：1,2-ジメトキシエタン

MEP：リン酸メチルエチレン

[0022] LiPF6 of the amount which serves as concentration of 1.0 mols/l. at the mixed solvent which made example 3EC, a dimethyl carbonate (DMC), and capacity % of MEP 40 capacity %, ten capacity %, and 50 capacity % Self-extinguishing and electric conductivity were measured about the electrolytic solution which dissolved. A result is shown in Table 2.
[0023] LiPF6 of the amount which serves as concentration of 1.0 mols/l. at the mixed solvent which made capacity % of example 4EC, and DMC and MEP 60 capacity %, ten capacity %, and 30 capacity % Self-extinguishing and electric conductivity were measured about the electrolytic solution which dissolved. A result is shown in Table 2.
[0024] LiPF6 of the amount which serves as concentration of 1.0 mols/l. at the mixed solvent which made capacity % of example of comparison 3EC, and DME and MEP 80 capacity %, ten capacity %, and ten capacity % Self-extinguishing and electric conductivity were measured about the electrolytic solution which dissolved. A result is shown in Table 2.
[0025] the example 4 of comparison — LiPF6 of the amount which serves as concentration of 1.0 mols/l. at the mixed solvent which made capacity % of EC and DMC 90 capacity % and ten capacity % Self-extinguishing and electric conductivity were measured about the electrolytic solution which dissolved. A result is shown in Table 2.
[0026]
[Table 2]

表　2

	混合溶媒			評価	
	EC (容積%)	DMC (容積%)	MEP (容積%)	自己消火性	電導度 (mS/cm)
実施例3	40	10	50	1秒以内に消火	6.2
実施例4	60	10	30	1秒以内に消火	6.4
比較例3	80	10	10	消火せず	6.3
比較例4	90	10	0	消火せず	9.2

EC：エチレンカーボネート

DMC：炭酸ジメチル

MEP：リン酸メチルエチレン

[0027] LiPF6 of the amount which serves as concentration of 1.0 mols/l. at example 5EC, a propylene carbonate (PC), and the mixed solvent that made capacity % of MEP 40 capacity %, ten capacity %, and 50 capacity % Self-extinguishing and electric conductivity were measured about the electrolytic solution which dissolved. A result is shown in Table 3.
[0028] LiPF6 of the amount which serves as concentration of 1.0 mols/l. at the mixed solvent which made capacity % of example 6EC, and PC and MEP 60 capacity %, ten capacity %, and 30 capacity % Self-extinguishing and electric conductivity were measured about the electrolytic solution which dissolved. A result is shown in Table 3.
[0029] LiPF6 of the amount which serves as concentration of 1.0 mols/l. at the mixed solvent which made capacity %

of example of comparison 5EC, and PC and MEP 80 capacity %, ten capacity %, and ten capacity % Self-extinguishing and electric conductivity were measured about the electrolytic solution which dissolved. A result is shown in Table 3.
[0030] the example 6 of comparison — LiPF6 of the amount which serves as concentration of 1.0 mols/l. at the mixed solvent which made capacity % of EC and PC 90 capacity % and ten capacity % Self-extinguishing and electric conductivity were measured about the electrolytic solution which dissolved. A result is shown in Table 3.
[0031]
[Table 3]

表　3

	混合溶媒			評価	
	EC (容積%)	PC (容積%)	MEP (容積%)	自己消火性	電導度 (mS/cm)
実施例5	40	10	50	1秒以内に消火	5.7
実施例6	60	10	30	1秒以内に消火	5.9
比較例5	80	10	10	消火せず	5.7
比較例6	90	10	0	消火せず	8.3

EC：エチレンカーボネート

PC：炭酸プロピレン

MEP：リン酸メチルエチレン

[0032] an example 7 — LiPF6 of the amount which serves as concentration of 1.0 mols/l. at the mixed solvent which made each capacity % of EC, DME, and phosphoric-acid ethyl ethylene (EEP) 40 capacity %, ten capacity %, and 50 capacity % Self-extinguishing and electric conductivity were measured about the electrolytic solution which dissolved. A result is shown in Table 4.
[0033] LiPE6 of the amount which serves as concentration of 1.0 mols/l. at the mixed solvent which made capacity % of example 8EC, and DME and EEP 60 capacity %, ten capacity %, and 30 capacity % Self-extinguishing and electric conductivity were measured about the electrolytic solution which dissolved. A result is shown in Table 4.
[0034] LiPF6 of the amount which serves as concentration of 1.0 mols/l. at the mixed solvent which made capacity % of example of comparison 7EC, and DME and EEP 80 capacity %, ten capacity %, and ten capacity % Self-extinguishing and electric conductivity were measured about the electrolytic solution which dissolved. A result is shown in Table 4.
[0035]
[Table 4]
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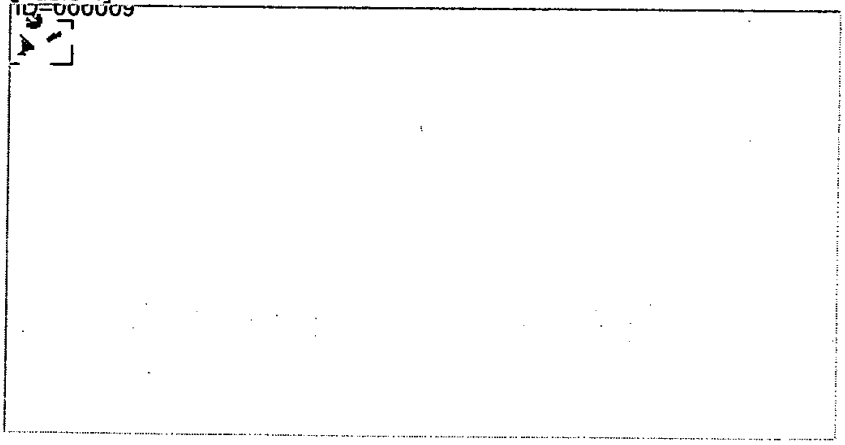

[0036]
[Effect of the Invention] As for the electrolytic solution, self-extinguishing is given by making the cyclic-phosphoric-acid ester which has self-extinguishing contain in the electrolytic solution. In the case of electrolytic-solution disclosure, danger of the lithium cell using this electrolytic solution, such as ignition destruction by fire, disappears, and its safety improves.

[Translation done.]

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TECHNICAL FIELD

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[Translation done.]

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1. This document has been translated by computer.So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3.In the drawings, any words are not translated.

PRIOR ART

[Description of the Prior Art] In recent years, the lithium cell using the organic-solvent electrolytic solution is widely used as a power supply of high-energy density with the miniaturization of electronic equipment, and carrying-izing. This organic-solvent electrolytic solution is a low viscosity solvent to an ethylene carbonate, a propylene carbonate, gamma-butyrolactone, etc. as a high dielectric constant solvent. the solvent which mixed dimethyl-carbonate, ethyl-carbonate methyl, diethyl carbonate, 1, and 2-dimethoxyethane etc. — a solute (electrolyte) LiPF6, LiBF4, LiCF3 SO3, and LiN (CF3 SO2)2 etc. — what mixed lithium salt is used

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EFFECT OF THE INVENTION

[Effect of the Invention] As for the electrolytic solution, self-extinguishing is given by making the annular phosphoric ester which has self-extinguishing contain in the electrolytic solution. In the case of electrolytic-solution disclosure, danger of the lithium cell using this electrolytic solution, such as ignition destruction by fire, disappears, and its safety improves.

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] The solvent currently used for such the electrolytic solution is an inflammable inflammable high solvent, and when the electrolytic solution spills liquid by the pressure buildup inside a cell, or mechanical destruction of a cell, it has the danger of carrying out ignition combustion. Moreover, development of the object for power storage or the large-sized cell for electric vehicles is also furthered, and the safe disposition top, such as flameproofing of the electrolytic solution, is called for. this invention solves the above technical problem and aims at offer of the organic-solvent electrolytic solution which has self-extinguishing.

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MEANS

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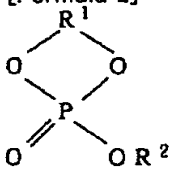

(1)

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OPERATION

[Function] Cyclic-phosphoric-acid ester has self-extinguishing, and gives self-extinguishing to the electrolytic solution for lithium cells by making the electrolytic solution contain.
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[Embodiments of the Invention]
Lithium salt as a solute: As the electrolyte used for the electrolytic solution of this invention LiPF6, LiBF4, LiClO4, LiAsF6, and LiSbF6, LiCF3 SO3, LiN (CF3 SO2)2, and LiN (CF3 CF2 SO2)2, LiN (CF3 SO2) (CF3 3 (CF2) SO2), LiN (CF3 3 (CF2) SO2)2, LiC (CF3 SO2)3, and LiC (CF3 CF2 SO2)3 etc. — lithium salt can be used The lithium salt concentration in the electrolytic solution can be used by the 0.1-1.5 mols [/l.] density range.
[0009] Mixed solvent: It is cyclic-phosphoric-acid ester shown by the (a) formula (1) as a solvent in this invention.
[0010]
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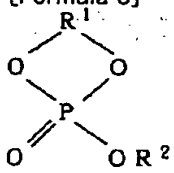

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The mixed solvent containing 20 to 55 capacity %, and the (b) annular carbonate 10 - 80 capacity % is used.
(a) Cyclic-phosphoric-acid ester : an autolysis-slaking operation of cyclic-phosphoric-acid ester (a) is the alkylene machine R1, so that there are few the carbon and the hydrogen contents in cyclic-phosphoric-acid ester. And alkyl group R2 It is so large that it is small. Therefore, alkylene machine R1 2-8 pieces are desirable and a carbon number is an alkyl group R2. 1-4 pieces of a carbon number are desirable. Alkylene machine R1 If it carries out, an ethylene, a propylene machine, a trimethylene machine, a butylene machine, an isobutylene machine, a tetramethylen machine, a pentamethylene machine, a trimethylethylene machine, a hexamethylene machine, a tetramethyl ethylene, a heptamethylene machine, an octamethylene machine, etc. are mentioned. Moreover, alkyl group R2 If it carries out, a methyl group, an ethyl group, n-propyl group, an isopropyl machine, n-butyl, a sec-butyl, t-butyl, an isobutyl machine, etc. are mentioned.
[0012] As an example of cyclic-phosphoric-acid ester (a), it is a phosphoric-acid ethylene methyl. Phosphoric-acid ethylene ethyl, a phosphoric-acid ethylene-n-propyl, a phosphoric-acid ethylene isopropyl, Phosphoric-acid ethylene-n-butyl, phosphoric-acid ethylene-sec-butyl, phosphoric-acid ethylene-t-butyl, A phosphoric-acid propylene methyl, phosphoric-acid propylene ethyl, a phosphoric-acid propylene-n-propyl, A phosphoric-acid propylene isopropyl, phosphoric-acid propylene-n-butyl, phosphoric-acid propylene-sec-butyl, Phosphoric-acid propylene-t-butyl, a phosphoric-acid trimethylene methyl, phosphoric-acid trimethylene ethyl, A phosphoric-acid trimethylene-n-propyl, a phosphoric-acid trimethylene isopropyl, Phosphoric-acid trimethylene-n-butyl, phosphoric-acid trimethylene-sec-butyl, Phosphoric-acid trimethylene-t-butyl, a phosphoric-acid butylene methyl, phosphoric-acid butylene ethyl, A phosphoric-acid butylene-n-propyl, a phosphoric-acid butylene isopropyl, phosphoric-acid butylene-n-butyl, Phosphoric-acid butylene-sec-butyl, phosphoric-acid butylene-t-butyl, A phosphoric-acid isobutylene methyl, phosphoric-acid isobutylene ethyl, a phosphoric-acid isobutylene-n-propyl, A phosphoric-acid isobutylene isopropyl, phosphoric-acid isobutylene-n-butyl, Phosphoric-acid isobutylene-sec-butyl, phosphoric-acid isobutylene-t-butyl, Phosphoric-acid tetramethylen memory, phosphoric-acid tetramethylen ethyl, a phosphoric-acid tetramethylen-n-propyl, A phosphoric-acid tetramethylen isopropyl, phosphoric-acid tetramethylen-n-butyl, Phosphoric-acid tetramethylen-sec-butyl, phosphoric-acid tetramethylen-t-butyl, A phosphoric-acid pentamethylene methyl, phosphoric-acid pentamethylene ethyl, a phosphoric-acid pentamethylene-n-propyl, A phosphoric-acid pentamethylene isopropyl, phosphoric-acid pentamethylene-n-butyl, Phosphoric-acid pentamethylene-sec-butyl, phosphoric-acid pentamethylene-t-butyl, A phosphoric-acid trimethylethylene methyl, phosphoric-acid trimethylethylene ethyl, A phosphoric-acid trimethylethylene-n-propyl, a phosphoric-acid trimethylethylene isopropyl, Phosphoric-acid trimethylethylene-n-butyl, phosphoric-acid trimethylethylene-sec-butyl, Phosphoric-acid trimethylethylene-t-butyl, a phosphoric-acid hexamethylene methyl, Phosphoric-acid hexamethylene ethyl, a phosphoric-acid hexamethylene-n-propyl, A phosphoric-acid hexamethylene isopropyl, phosphoric-acid hexamethylene-n-butyl, Phosphoric-acid hexamethylene-sec-butyl, phosphoric-acid hexamethylene-t-butyl, A phosphoric-acid tetramethyl ethylene methyl, phosphoric-acid tetramethyl ethylene ethyl, A phosphoric-acid tetramethyl ethylene-n-propyl, a phosphoric-acid tetramethyl ethylene isopropyl, Phosphoric-acid tetramethyl ethylene-n-butyl, phosphoric-acid tetramethyl ethylene-sec-butyl, Phosphoric-acid tetramethyl ethylene-t-butyl, a phosphoric-acid heptamethylene methyl, Phosphoric-acid heptamethylene ethyl, a phosphoric-acid heptamethylene-n-propyl, A phosphoric-acid heptamethylene isopropyl, phosphoric-acid heptamethylene-n-butyl, Phosphoric-acid heptamethylene-sec-butyl, phosphoric-acid heptamethylene-t-butyl, A phosphoric-acid octamethylene methyl, phosphoric-acid octamethylene ethyl, a phosphoric-acid octamethylene-n-propyl, A phosphoric-acid octamethylene isopropyl, phosphoric-acid octamethylene n-butyl, phosphoric-acid octamethylene-sec-butyl, phosphoric-acid octamethylene-t-butyl, etc. are mentioned. These are

independent, or two or more sorts can be mixed and they can be used.
[0013] (b) Annular carbonate : as an annular carbonate, an ethylene carbonate, a propylene carbonate, a carbonic acid butylene, a carbonic acid isobutylene, carbonic acid trimethylene, a carbonic acid trimethylethylene, carbonic acid tetramethyl ethylene, dimethyl-carbonate trimethylene, etc. are mentioned. These are independent, or two or more sorts can be mixed and they can be used.
[0014] (c) Other solvents : out of using cyclic-phosphoric-acid ester (a) and an annular carbonate (b) as a mixed solvent, you may mix and use solvents other than cyclic-phosphoric-acid ester and an annular carbonate (c) for the improvement in electric conductivity of the electrolytic solution. solvent 5-15 capacity % In this case, as for the amount of cyclic-phosphoric-acid ester, 20 to 55 capacity % and 30 to annular carbonate 75 capacity %, and (c) others should just be contained. By making it such a range, electric conductivity is high and can obtain the electrolytic solution for lithium cells which was excellent in self-extinguishing.
[0015] As solvents other than cyclic-phosphoric-acid ester and an annular carbonate A dimethyl carbonate, an ethyl-carbonate methyl, diethyl carbonate, a carbonic acid dipropyl, A carbonic acid diisopropyl, carbonic acid methylpropyl, a methyl carbonate isopropyl, Chain-like carbonates, such as an ethyl-carbonate propyl and an ethyl-carbonate isopropyl 1, 2-dimethoxyethane, 1, 2-diethoxy ethane, 1-ethoxy-2-methoxyethane, Chain-like ether, such as 1, 2-dipropoxy ethane, 1, 2-JIISO propoxy ethane, 1, and 2-dibutoxy ethane, A tetrahydrofuran, a methyl tetrahydrofuran, a tetrahydropyran, Cyclic ether, such as a methyl tetrahydropyran and a dioxane, methyl acetate, Ethyl acetate, propyl acetate, a methyl propionate, an ethyl propionate, Carboxylates, such as gamma-butyrolactone, beta-butyrolactone, delta-valerolactone, and gamma-valerolactone Amides, such as a dimethylformamide and a dimethylacetamide, a sulfurous-acid dimethyl, Sulfites, such as a sulfurous-acid diethyl, sulfurous-acid ethylene, and a sulfurous-acid propylene Sulfates, such as a dimethyl sulfate, a diethyl sulfate, sulfuric-acid ethylene, and a sulfuric-acid propylene, It is independent, or two or more sorts can be mixed and nitril, such as sulfones, such as sulfoxides, such as dimethyl sulfoxide and a diethyl sulfoxide, a dimethyl sulfone, a diethyl sulfone, and a sulfolane, an acetonitrile, and a propionitrile, can also be used. 1, 2-dimethoxyethane, and a dimethyl carbonate are desirable also in these.

[Translation done.]

EXAMPLE

[Example] Hereafter, an example explains this invention in detail. In addition, evaluation is based on the following method.
10 minutes or more were dipped in the beaker into which the electrolytic solution went the glass fiber filter paper of the shape of a strip of paper with self-extinguishing evaluation of the electrolytic solution and electric conductivity measurement width of face of 15mm, a length [of 300mm], and a thickness of 0.19mm. Except for the superfluous electrolytic solution, the end of a glass fiber filter paper was gathered with a clip from the glass fiber filter paper on the edge of a beaker, and it hung to the perpendicular. Time until it lights and carries out autolysis slaking to this soffit with a writer was measured. Moreover, about the electric conductivity (25 degrees C) of the electrolytic solution, it measured using the electric conductivity meter.
[0017] LiPF6 of the amount which serves as concentration of 1.0 mols/l. at the mixed solvent which made each capacity % of example 1 ethylene carbonate (EC), 1, 2-dimethoxyethane (DME), and a phosphoric-acid methyl ethylene (MEP) 40 capacity %, ten capacity %, and 50 capacity % Self-extinguishing and electric conductivity were measured about the electrolytic solution which dissolved. A result is shown in Table 1.
[0018] LiPF6 of the amount which serves as concentration of 1.0 mols/l. at the mixed solvent which made capacity % of example 2EC, and DME and MEP 60 capacity %, ten capacity %, and 30 capacity % Self-extinguishing and electric conductivity were measured about the electrolytic solution which dissolved. A result is shown in Table 1.
[0019] LiPF6 of the amount which serves as concentration of 1.0 mols/l. at the mixed solvent which made capacity % of example of comparison 1EC, and DME and MEP 80 capacity %, ten capacity %, and ten capacity % Self-extinguishing and electric conductivity were measured about the electrolytic solution which dissolved. A result is shown in Table 1.
[0020] the example 2 of comparison -- LiPF6 of the amount which serves as concentration of 1.0 mols/l. at the mixed solvent which made capacity % of EC and DME 90 capacity % and ten capacity % Self-extinguishing and electric conductivity were measured about the electrolytic solution which dissolved. A result is shown in Table 1.
[0021]
[Table 1]

表　1

	混合溶媒			評価	
	EC (容積%)	DME (容積%)	MEP (容積%)	自己消火性	電導度 (mS/cm)
実施例1	40	10	50	1秒以内に消火	6.9
実施例2	60	10	30	3秒で消火	7.1
比較例1	80	10	10	消火せず	7.5
比較例2	90	10	0	消火せず	10.6

EC：エチレンカーボネート

DME：1,2-ジメトキシエタン

MEP：リン酸メチルエチレン

[0022] LiPF6 of the amount which serves as concentration of 1.0 mols/l. at the mixed solvent which made example 3EC, a dimethyl carbonate (DMC), and capacity % of MEP 40 capacity %, ten capacity %, and 50 capacity % Self-extinguishing and electric conductivity were measured about the electrolytic solution which dissolved. A result is shown in Table 2.
[0023] LiPF6 of the amount which serves as concentration of 1.0 mols/l. at the mixed solvent which made capacity % of example 4EC, and DMC and MEP 60 capacity %, ten capacity %, and 30 capacity % Self-extinguishing and electric conductivity were measured about the electrolytic solution which dissolved. A result is shown in Table 2.
[0024] LiPF6 of the amount which serves as concentration of 1.0 mols/l. at the mixed solvent which made capacity % of example of comparison 3EC, and DME and MEP 80 capacity %, ten capacity %, and ten capacity % Self-extinguishing and electric conductivity were measured about the electrolytic solution which dissolved. A result is shown in Table 2.
[0025] the example 4 of comparison -- LiPF6 of the amount which serves as concentration of 1.0 mols/l. at the mixed solvent which made capacity % of EC and DMC 90 capacity % and ten capacity % Self-extinguishing and electric conductivity were measured about the electrolytic solution which dissolved. A result is shown in Table 2.
[0026]
[Table 2]

表　2

	混合溶媒			評価	
	EC（容積%）	DMC（容積%）	MEP（容積%）	自己消火性	電導度（mS/cm）
実施例3	40	10	50	1秒以内に消火	6.2
実施例4	60	10	30	1秒以内に消火	6.4
比較例3	80	10	10	消火せず	6.3
比較例4	90	10	0	消火せず	9.2

EC：エチレンカーボネート

DMC：炭酸ジメチル

MEP：リン酸メチルエチレン

[0027] LiPF6 of the amount which serves as concentration of 1.0 mols/l. at example 5EC, a propylene carbonate (PC), and the mixed solvent that made capacity % of MEP 40 capacity %, ten capacity %, and 50 capacity % Self-extinguishing and electric conductivity were measured about the electrolytic solution which dissolved. A result is shown in Table 3.
[0028] LiPF6 of the amount which serves as concentration of 1.0 mols/l. at the mixed solvent which made capacity % of example 6EC, and PC and MEP 60 capacity %, ten capacity %, and 30 capacity % Self-extinguishing and electric conductivity were measured about the electrolytic solution which dissolved. A result is shown in Table 3.
[0029] LiPF6 of the amount which serves as concentration of 1.0 mols/l. at the mixed solvent which made capacity % of example of comparison 5EC, and PC and MEP 80 capacity %, ten capacity %, and ten capacity % Self-extinguishing and electric conductivity were measured about the electrolytic solution which dissolved. A result is shown in Table 3.
[0030] the example 6 of comparison -- LiPF6 of the amount which serves as concentration of 1.0 mols/l. at the mixed solvent which made capacity % of EC and PC 90 capacity % and ten capacity % Self-extinguishing and electric conductivity were measured about the electrolytic solution which dissolved. A result is shown in Table 3.
[0031]
[Table 3]

表　3

	混合溶媒			評価	
	EC（容積%）	PC（容積%）	MEP（容積%）	自己消火性	電導度（mS/cm）
実施例5	40	10	50	1秒以内に消火	5.7
実施例6	60	10	30	1秒以内に消火	5.9
比較例5	80	10	10	消火せず	5.7
比較例6	90	10	0	消火せず	8.3

EC：エチレンカーボネート

PC：炭酸プロピレン

MEP：リン酸メチルエチレン

[0032] an example 7 -- LiPF6 of the amount which serves as concentration of 1.0 mols/l. at the mixed solvent which made each capacity % of EC, DME, and phosphoric-acid ethyl ethylene (EEP) 40 capacity %, ten capacity %, and 50 capacity % Self-extinguishing and electric conductivity were measured about the electrolytic solution which dissolved. A result is shown in Table 4.
[0033] LiPE6 of the amount which serves as concentration of 1.0 mols/l. at the mixed solvent which made capacity % of example 8EC, and DME and EEP 60 capacity %, ten capacity %, and 30 capacity % Self-extinguishing and electric conductivity were measured about the electrolytic solution which dissolved. A result is shown in Table 4.
[0034] LiPF6 of the amount which serves as concentration of 1.0 mols/l. at the mixed solvent which made capacity % of example of comparison 7EC, and DME and EEP 80 capacity %, ten capacity %, and ten capacity % Self-extinguishing and electric conductivity were measured about the electrolytic solution which dissolved. A result is shown in Table 4.
[0035]
[Table 4]

表　4

	混合溶媒			評価	
	EC（容積%）	DME（容積%）	EEP（容積%）	自己消火性	電導度（mS/cm）
実施例7	40	10	50	1秒以内に消火	7.0
実施例8	60	10	30	3秒で消火	7.2
比較例7	80	10	10	消火せず	7.6

EC：エチレンカーボネート

DME：1.2-ジメトキシエタン

EEP：リン酸メチルエチレン

[Translation done.]

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(71)出願人　000005968
三菱化学株式会社
東京都千代田区丸の内二丁目５番２号

(72)発明者　島　邦久
茨城県稲敷郡阿見町中央８丁目３番１号
三菱化学株式会社筑波研究所内

(72)発明者　石垣　憲一
茨城県稲敷郡阿見町中央８丁目３番１号
三菱化学株式会社筑波研究所内

(72)発明者　安川　栄起
茨城県稲敷郡阿見町中央８丁目３番１号
三菱化学株式会社筑波研究所内

(74)代理人　弁理士　長谷川　曉司

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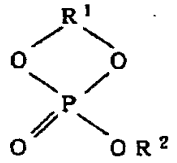
(54)【発明の名称】　リチウム電池用電解液

(57)【要約】

【課題】　自己消火性を有し、安全性に優れたリチウム電池用電解液の提供。

【解決手段】　溶質のリチウム塩を、（ａ）式（１）で示される環状リン酸エステル

【化１】



（１）

〔式中、R^1 は炭素数２～８のアルキレン基を表し、R^2 は炭素数１～４のアルキル基を表す。〕

２０～５５容積％および（ｂ）環状炭酸エステル１０～８０容積％を含有する混合溶媒に溶解したリチウム電池用電解液。

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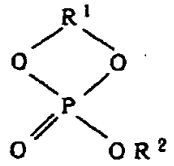
【特許請求の範囲】

【請求項１】　溶質のリチウム塩を、（ａ）式（１）で示される環状リン酸エステル

【化１】



（１）

〔式中、R^1 は炭素数２～８のアルキレン基を表し、R^2 は炭素数１～４のアルキル基を表す。〕

２０～５５容積％および（ｂ）環状炭酸エステル：１０～８０容積％を含有する混合溶媒に溶解したリチウム電池用電解液。

【請求項２】　環状炭酸エステル（ｂ）が、炭酸エチレン、炭酸プロピレンより選ばれた化合物である請求項１記載のリチウム電池用分解液。

【請求項３】　式（１）で示される環状リン酸エステル（ａ）が、リン酸メチルエチレン、リン酸エチルエチレンより選ばれた化合物である、請求項１記載のリチウム電池用電解液。

【請求項４】　混合溶媒は、（ａ）式（１）で示される環状リン酸エステル２０～５５容積％、（ｂ）環状炭酸エステル３０～７５容積％および（ｃ）１，２－ジメトキシエタンおよび炭酸ジメチルより選ばれた化合物５～１５容積％の混合物である、請求項１記載のリチウム電池用電解液。

【請求項５】　溶質のリチウム塩が、$LiPF_6$ である、請求項１記載のリチウム電池用電解液。

【発明の詳細な説明】

【０００１】

【発明の属する技術分野】本発明は、自己消火性を有し、安全性に優れたリチウム電池用電解液に関するものである。

【０００２】

【従来の技術】近年、電子機器の小型化、携帯化にともない、有機溶媒電解液を用いたリチウム電池が高エネルギー密度の電源として広く用いられている。この有機溶媒電解液は、高誘電率溶媒として炭酸エチレン、炭酸プロピレン、γ-ブチロラクトンなどに、低粘性溶媒として炭酸ジメチル、炭酸エチルメチル、炭酸ジエチル、１，２－ジメトキシエタンなどを混合した溶媒に、溶質（電解質）$LiPF_6$、$LiBF_4$、$LiCF_3SO_3$、$LiN(CF_3SO_2)_2$ などのリチウム塩を混合したものが用いられている。

【０００３】

【発明が解決しようとする課題】このような電解液に使用されている溶媒は引火性の高い可燃性溶媒であり、電池内部の圧力上昇または電池の機械的破壊により電解液

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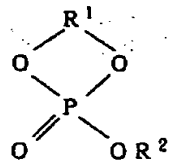
が漏液した場合、引火燃焼する危険性がある。また、電力貯蔵用あるいは電気自動車用大型電池の開発も進められており、電解液の難燃化などの安全性向上が求められている。本発明は、以上の課題を解決するものであり、自己消火性を有する有機溶媒電解液の提供を目的とする。

【０００４】

【課題を解決するための手段】本発明は、溶質としてリチウム塩を、（ａ）式（１）で示される環状リン酸エステル

【０００５】

【化２】



（１）

【０００６】〔式中、R^1 は炭素数２～８のアルキレン基を表し、R^2 は炭素数１～４のアルキル基を表す。〕２０～５５容積％および（ｂ）環状炭酸エステル１０～８０容積％を含有する混合溶媒に溶解したリチウム電池用電解液を提供するものである。

【０００７】

【作用】環状リン酸エステルは自己消火性を有し、電解液に含有させることによりリチウム電池用電解液に自己消火性を付与する。

【０００８】

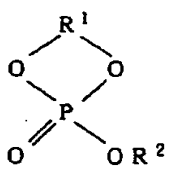
【発明の実施の形態】

溶質としてのリチウム塩：本発明の電解液に用いる電解質としては、$LiPF_6$、$LiBF_4$、$LiClO_4$、$LiAsF_6$、$LiSbF_6$、$LiCF_3SO_3$、$LiN(CF_3SO_2)_2$、$LiN(CF_3CF_2SO_2)_2$、$LiN(CF_3SO_2)(CF_3(CF_2)_3SO_2)$、$LiN(CF_3(CF_2)_3SO_2)_2$、$LiC(CF_3SO_2)_3$、$LiC(CF_3CF_2SO_2)_3$ などのリチウム塩を使用することができる。電解液中のリチウム塩濃度は、０．１～１．５モル／リットルの濃度範囲で用いることができる。

【０００９】混合溶媒：本発明において、溶媒としては、（ａ）式（１）で示される環状リン酸エステル

【００１０】

【化３】



（１）

【００１１】〔式中、R^1 は炭素数２～８のアルキレン

基を表し、R^2 は炭素数１～４のアルキル基を表す。］２０～５５容積％および（ｂ）環状炭酸エステル１０～８０容積％を含有する混合溶媒が用いられる。

（ａ）環状リン酸エステル：環状リン酸エステル（ａ）の自己消火作用は、環状リン酸エステル中の炭素及び水素含量が少ないほど、すなわちアルキレン基R^1及びアルキル基R^2が小さいほど大きい。したがって、アルキレン基R^1の炭素数は２～８個が好ましく、アルキル基R^2の炭素数は１～４個が好ましい。アルキレン基R^1としては、エチレン基、プロピレン基、トリメチレン基、ブチレン基、イソブチレン基、テトラメチレン基、ペンタメチレン基、トリメチルエチレン基、ヘキサメチレン基、テトラメチルエチレン基、ヘプタメチレン基、オクタメチレン基などが挙げられる。また、アルキル基R^2としては、メチル基、エチル基、ｎ－プロピル基、イソプロピル基、ｎ－ブチル基、ｓｅｃ－ブチル基、ｔ－ブチル基、イソブチル基などが挙げられる。

【００１２】環状リン酸エステル（ａ）の具体例としては、リン酸エチレンメチル、リン酸エチレンエチル、リン酸エチレン－ｎ－プロピル、リン酸エチレンイソプロピル、リン酸エチレン－ｎ－ブチル、リン酸エチレン－ｓｅｃ－ブチル、リン酸エチレン－ｔ－ブチル、リン酸プロピレンメチル、リン酸プロピレンエチル、リン酸プロピレン－ｎ－プロピル、リン酸プロピレンイソプロピル、リン酸プロピレン－ｎ－ブチル、リン酸プロピレン－ｓｅｃ－ブチル、リン酸プロピレン－ｔ－ブチル、リン酸トリメチレンメチル、リン酸トリメチレンエチル、リン酸トリメチレン－ｎ－プロピル、リン酸トリメチレンイソプロピル、リン酸トリメチレン－ｎ－ブチル、リン酸トリメチレン－ｓｅｃ－ブチル、リン酸トリメチレン－ｔ－ブチル、リン酸ブチレンメチル、リン酸ブチレンエチル、リン酸ブチレン－ｎ－プロピル、リン酸ブチレンイソプロピル、リン酸ブチレン－ｎ－ブチル、、リン酸ブチレン－ｓｅｃ－ブチル、リン酸ブチレン－ｔ－ブチル、リン酸イソブチレンメチル、リン酸イソブチレンエチル、リン酸イソブチレン－ｎ－プロピル、リン酸イソブチレンイソプロピル、リン酸イソブチレン－ｎ－ブチル、リン酸イソブチレン－ｓｅｃ－ブチル、リン酸イソブチレン－ｔ－ブチル、リン酸テトラメチレンメモリ、リン酸テトラメチレンエチル、リン酸テトラメチレン－ｎ－プロピル、リン酸テトラメチレンイソプロピル、リン酸テトラメチレン－ｎ－ブチル、リン酸テトラメチレン－ｓｅｃ－ブチル、リン酸テトラメチレン－ｔ－ブチル、リン酸ペンタメチレンメチル、リン酸ペンタメチレンエチル、リン酸ペンタメチレン－ｎ－プロピル、リン酸ペンタメチレンイソプロピル、リン酸ペンタメチレン－ｎ－ブチル、リン酸ペンタメチレン－ｓｅｃ－ブチル、リン酸ペンタメチレン－ｔ－ブチル、リン酸トリメチルエチレンメチル、リン酸トリメチルエチレンエチル、リン酸トリメチルエチレン－ｎ－プロピル、リン酸トリメチルエチレンイソプロピル、リン酸トリメチルエチレン－ｎ－ブチル、リン酸トリメチルエチレン－ｓｅｃ－ブチル、リン酸トリメチルエチレン－ｔ－ブチル、リン酸ヘキサメチレンメチル、リン酸ヘキサメチレンエチル、リン酸ヘキサメチレン－ｎ－プロピル、リン酸ヘキサメチレンイソプロピル、リン酸ヘキサメチレン－ｎ－ブチル、リン酸ヘキサメチレン－ｓｅｃ－ブチル、リン酸ヘキサメチレン－ｔ－ブチル、リン酸テトラメチルエチレンメチル、リン酸テトラメチルエチレンエチル、リン酸テトラメチルエチレン－ｎ－プロピル、リン酸テトラメチルエチレンイソプロピル、リン酸テトラメチルエチレン－ｎ－ブチル、リン酸テトラメチルエチレン－ｓｅｃ－ブチル、リン酸テトラメチルエチレン－ｔ－ブチル、リン酸ヘプタメチレンメチル、リン酸ヘプタメチレンエチル、リン酸ヘプタメチレン－ｎ－プロピル、リン酸ヘプタメチレンイソプロピル、リン酸ヘプタメチレン－ｎ－ブチル、リン酸ヘプタメチレン－ｓｅｃ－ブチル、リン酸ヘプタメチレン－ｔ－ブチル、リン酸オクタメチレンメチル、リン酸オクタメチレンエチル、リン酸オクタメチレン－ｎ－プロピル、リン酸オクタメチレンイソプロピル、リン酸オクタメチレンｎ－ブチル、リン酸オクタメチレン－ｓｅｃ－ブチル、リン酸オクタメチレン－ｔ－ブチルなどが挙げられる。これらは単独で、または２種以上混合して用いることができる。

【００１３】（ｂ）環状炭酸エステル：環状炭酸エステルとしては、炭酸エチレン、炭酸プロピレン、炭酸ブチレン、炭酸イソブチレン、炭酸トリメチレン、炭酸トリメチルエチレン、炭酸テトラメチルエチレン、炭酸ジメチルトリメチレンなどが挙げられる。これらは単独で、または２種以上混合して用いることができる。

【００１４】（ｃ）他の溶媒：環状リン酸エステル（ａ）及び環状炭酸エステル（ｂ）を混合溶媒として使用することの外に、電解液の電導度向上のため環状リン酸エステル及び環状炭酸エステル以外の溶媒（ｃ）を混合して用いてもよい。この場合、環状リン酸エステルの量は２０～５５容積％、また環状炭酸エステル３０～７５容積％、（ｃ）他の溶媒５～１５容積％含まれていればよい。このような範囲にすることにより、電導度が高く、かつ自己消火性の優れたリチウム電池用電解液を得ることができる。

【００１５】環状リン酸エステル及び環状炭酸エステル以外の溶媒としては、炭酸ジメチル、炭酸エチルメチル、炭酸ジエチル、炭酸ジプロピル、炭酸ジイソプロピル、炭酸メチルプロピル、炭酸メチルイソプロピル、炭酸エチルプロピル、炭酸エチルイソプロピルなどの鎖状炭酸エステル類、１，２－ジメトキシエタン、１，２－ジエトキシエタン、１－エトキシ－２－メトキシエタン、１，２－ジプロポキシエタン、１，２－ジイソプロポキシエタン、１，２－ジブトキシエタンなどの鎖状エーテル類、テトラヒドロフラン、メチルテトラヒドロフ

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ラン、テトラヒドロピラン、メチルテトラヒドロピラン、ジオキサンなどの環状エーテル類、酢酸メチル、酢酸エチル、酢酸プロピル、プロピオン酸メチル、プロピオン酸エチル、γ－ブチロラクトン、β－ブチロラクトン、δ－バレロラクトン、γ－バレロラクトンなどのカルボン酸エステル類、ジメチルホルムアミド、ジメチルアセトアミドなどのアミド類、亜硫酸ジメチル、亜硫酸ジエチル、亜硫酸エチレン、亜硫酸プロピレンなどの亜硫酸エステル類、硫酸ジメチル、硫酸ジエチル、硫酸エチレン、硫酸プロピレンなどの硫酸エステル、ジメチルスルホキシド、ジエチルスルホキシドなどのスルホキシド類、ジメチルスルホン、ジエチルスルホン、スルホランなどのスルホン類、アセトニトリル、プロピオニトリルなどのニトリル類を単独で、または２種以上混合して用いることもできる。これらの中でも１，２－ジメトキシエタン、炭酸ジメチルが好ましい。

【００１６】

【実施例】以下、実施例により本発明を詳細に説明する。なお、評価は次の方法による。

電解液の自己消火性評価及び電導度測定

幅１５mm、長さ３００mm、厚さ０．１９mmの短冊状のガラス繊維濾紙を電解液の入ったビーカーに１０分以上を浸した。ビーカーの縁でガラス繊維濾紙から過剰の電解液を除き、ガラス繊維濾紙の一端をクリップで摘み垂直に吊した。この下端にライターで着火し、自己消火するまでの時間を測定した。また、電解液の電導度（２５℃）については電導度計を用いて測定した。

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＊【００１７】実施例１

エチレンカーボネート（ＥＣ）、１，２－ジメトキシエタン（ＤＭＥ）、リン酸メチルエチレン（ＭＥＰ）の各々の容積％を、４０容積％、１０容積％、５０容積％とした混合溶媒に、濃度１．０モル／リットルとなる量のＬｉＰＦ$_6$ を溶解した電解液について、自己消火性及び電導度を測定した。結果を表１に示す。

【００１８】実施例２

ＥＣ、ＤＭＥ、ＭＥＰの各々の容積％を、６０容積％、１０容積％、３０容積％とした混合溶媒に、濃度１．０モル／リットルとなる量のＬｉＰＦ$_6$ を溶解した電解液について、自己消火性及び電導度を測定した。結果を表１に示す。

【００１９】比較例１

ＥＣ、ＤＭＥ、ＭＥＰの各々の容積％を、８０容積％、１０容積％、１０容積％とした混合溶媒に、濃度１．０モル／リットルとなる量のＬｉＰＦ$_6$ を溶解した電解液について、自己消火性及び電導度を測定した。結果を表１に示す。

【００２０】比較例２

ＥＣ、ＤＭＥの各々の容積％を、９０容積％、１０容積％とした混合溶媒に、濃度１．０モル／リットルとなる量のＬｉＰＦ$_6$ を溶解した電解液について、自己消火性及び電導度を測定した。結果を表１に示す。

【００２１】

【表１】

＊

表　１

	混合溶媒			評価	
	ＥＣ（容積％）	ＤＭＥ（容積％）	ＭＥＰ（容積％）	自己消火性	電導度（mS/cm）
実施例１	４０	１０	５０	１秒以内に消火	6.9
実施例２	６０	１０	３０	３秒で消火	7.1
比較例１	８０	１０	１０	消火せず	7.5
比較例２	９０	１０	０	消火せず	10.6

ＥＣ：エチレンカーボネート

ＤＭＥ：1.2-ジメトキシエタン

ＭＥＰ：リン酸メチルエチレン

【００２２】実施例３

ＥＣ、炭酸ジメチル（ＤＭＣ）、ＭＥＰの各々の容積％を、４０容積％、１０容積％、５０容積％とした混合溶媒に濃度１．０モル／リットルとなる量のＬｉＰＦ$_6$ を溶解した電解液について、自己消火性及び電導度を測定した。結果を表２に示す。

【００２３】実施例４

ＥＣ、ＤＭＣ、ＭＥＰの各々の容積％を、６０容積％、１０容積％、３０容積％とした混合溶媒に、濃度１．０モル／リットルとなる量のＬｉＰＦ$_6$ を溶解した電解液について、自己消火性及び電導度を測定した。結果を表２に示す。

【００２４】比較例３

ＥＣ、ＤＭＥ、ＭＥＰの各々の容積％を、８０容積％、１０容積％、１０容積％とした混合溶媒に、濃度１．０モル／リットルとなる量のＬｉＰＦ$_6$ を溶解した電解液について、自己消火性及び電導度を測定した。結果を表２に示す。

【００２５】比較例４

ＥＣ、ＤＭＣの各々の容積％を、９０容積％、１０容積％とした混合溶媒に濃度１．０モル／リットルとなる量のＬｉＰＦ$_6$ を溶解した電解液について、自己消火性及び電導度を測定した。結果を表２に示す。

【００２６】

【表２】

表　２

	混合溶媒			評価	
	ＥＣ（容積％）	ＤＭＣ（容積％）	ＭＥＰ（容積％）	自己消火性	電導度（mS/cm）
実施例３	４０	１０	５０	１秒以内に消火	6.2
実施例４	６０	１０	３０	１秒以内に消火	6.4
比較例３	８０	１０	１０	消火せず	6.3
比較例４	９０	１０	０	消火せず	9.2

ＥＣ：エチレンカーボネート

ＤＭＣ：炭酸ジメチル

ＭＥＰ：リン酸メチルエチレン

【００２７】実施例５

ＥＣ、炭酸プロピレン（ＰＣ）、ＭＥＰの各々の容積％を４０容積％、１０容積％、５０容積％とした混合溶媒に濃度１．０モル／リットルとなる量のＬｉＰＦ$_6$ を溶解した電解液について、自己消火性及び電導度を測定した。結果を表３に示す。

【００２８】実施例６

ＥＣ、ＰＣ、ＭＥＰの各々の容積％を、６０容積％、１０容積％、３０容積％とした混合溶媒に、濃度１．０モル／リットルとなる量のＬｉＰＦ$_6$ を溶解した電解液について、自己消火性及び電導度を測定した。結果を表３に示す。

【００２９】比較例５

※ＥＣ、ＰＣ、ＭＥＰの各々の容積％を、８０容積％、１０容積％、１０容積％とした混合溶媒に、濃度１．０モル／リットルとなる量のＬｉＰＦ$_6$ を溶解した電解液について、自己消火性及び電導度を測定した。結果を表３に示す。

【００３０】比較例６

ＥＣ、ＰＣの各々の容積％を，９０容積％、１０容積％とした混合溶媒に，濃度１．０モル／リットルとなる量のＬｉＰＦ$_6$ を溶解した電解液について、自己消火性及び電導度を測定した。結果を表３に示す。

【００３１】

【表３】

※

表　３

	混合溶媒			評価	
	ＥＣ（容積％）	ＰＣ（容積％）	ＭＥＰ（容積％）	自己消火性	電導度（mS/cm）
実施例５	４０	１０	５０	１秒以内に消火	5.7
実施例６	６０	１０	３０	１秒以内に消火	5.9
比較例５	８０	１０	１０	消火せず	5.7
比較例６	９０	１０	０	消火せず	8.3

ＥＣ：エチレンカーボネート

ＰＣ：炭酸プロピレン

ＭＥＰ：リン酸メチルエチレン

【００３２】実施例７

ＥＣ、ＤＭＥ、リン酸エチルエチレン（ＥＥＰ）の各々の容積％を、４０容積％、１０容積％、５０容積％とした混合溶媒に濃度１．０モル／リットルとなる量のＬｉＰＦ$_6$ を溶解した電解液について、自己消火性及び電導度を測定した。結果を表４に示す。

【００３３】実施例８

ＥＣ、ＤＭＥ、ＥＥＰの各々の容積％を、６０容積％、１０容積％、３０容積％とした混合溶媒に、濃度１．０モル／リットルとなる量のＬｉＰＥ$_6$ を溶解した電解液

について、自己消火性及び電導度を測定した。結果を表４に示す。

【００３４】比較例７

ＥＣ、ＤＭＥ、ＥＥＰの各々の容積％を８０容積％、１０容積％、１０容積％とした混合溶媒に、濃度１．０モル／リットルとなる量のＬｉＰＦ$_6$を溶解した電解液について、自己消火性及び電導度を測定した。結果を表４に示す。

【００３５】

【表４】

表　4

	混合溶媒			評価	
	ＥＣ（容積％）	ＤＭＥ（容積％）	ＥＥＰ（容積％）	自己消火性	電導度（mS/cm）
実施例７	４０	１０	５０	１秒以内に消火	7.0
実施例８	６０	１０	３０	３秒で消火	7.2
比較例７	８０	１０	１０	消火せず	7.6

ＥＣ：エチレンカーボネート

ＤＭＥ：1.2-ジメトキシエタン

ＥＥＰ：リン酸メチルエチレン

【００３６】

【発明の効果】自己消火性を有する環状リン酸エステルを電解液中に含有させることにより、電解液は自己消火性が付与される。この電解液を用いたリチウム電池は、電解液漏洩の際、着火炎上等の危険性がなくなり安全性が向上する。

フロントページの続き

(72)発明者　森　彰一郎

茨城県稲敷郡阿見町中央８丁目３番１号

三菱化学株式会社筑波研究所内